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POL Sensor Validation of SCAPS

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LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethyl benzene, and xylenes
EC	Degrees Celsius
Cal-EPA	California Environmental Protection Agency
cm	Centimeter
CPT	Cone Penetrometer System
C#	Carbon compound (the number proceeding 'C' indicates number of carbon atoms in compound)
DFM	Diesel fuel marine
DHS	Department of Health Services (California)
DOT	Department of Transportation
DTSC	Department of Toxic Substances Control
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Hcl	Hydrochloric acid
Hz	Hertz
IDW	Investigation Derived Waste
ITRC	Interstate Technology Regulatory and Cooperative Program
k	Thousand
kg	Kilograms
LIF	Laser-Induced Fluorescence
LNAPL	Light non-aqueous phase liquid
m	Meter
M	Million
mg	Milligram
min	Minute
mm	Millimeter
MTBE	Methyl Tertbutyl Ether
mm	Micron
NCCOSC	Naval Command Control and Oceanographic Surveillance Center
Nd:YAG	Neodymium:Yttrium Aluminum Garnet

NEX	Naval Exchange
nm	Nanometer

LIST OF ACRONYMS (continued)

NRaD	U.S. Department of the Navy, Naval Command, Control, and Ocean Surveillance Center, RDT&E Division
PNA	Polynuclear Aromatic Compound
PDA	Photodiode Array
POL	Petroleum, Oil, and Lubricant
ppm	Parts per million
RDTE	Research, Development, Test, and Evaluation
SCAPS	Site Characterization and Analysis Penetrometer System
SPAWAR	Space and Naval Warfare Systems Command
SSC	SPAWAR Systems Center
TPH	Total Petroleum Hydrocarbons
TRPH	Total Residual Petroleum Hydrocarbons
UV	Ultraviolet

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ACKNOWLEDGMENTS

The LIF sensing technologies demonstrated using the SCAPS were developed through a collaborative effort of the Navy, Army, and Air Force under the Tri-Service SCAPS program.

The SSC San Diego, formerly NCCOSC RDTE Division, performed the validation of the *in situ* LIF-based field screening technologies by using the SCAPS at over 15 sites. The SCAPS-LIF system is currently being either evaluated or demonstrated by several technology certification programs, including the following:

- Interstate Technology and Regulatory Cooperation Program (ITRC)
- California Environmental Protection Agency (Cal-EPA) - Technology Certification Program
- U.S. EPA, Department of Defense, and Department of Energy - Consortium for Site Characterization Technology
- Western Governor's Association - Committee to Develop On-Site Innovative Technologies

In addition, recognition goes to the individuals who contributed to the regulatory, technical, and policy issues of this document, including: Dr. Stephen Lieberman and Dr. David Knowles (SPAWAR Systems Center).

Technical material contained in this report has been approved for public release.
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1.0 EXECUTIVE SUMMARY

The ESTCP has established a program to accelerate acceptance and application of innovative monitoring and site characterization technologies. The LIF technologies using SCAPS platform provide quick and cost-effective real-time field screening of the physical and chemical characteristics of POL impacted sites. A secondary goal is the acquisition of geologic information while reducing the volume of IDW.

Each LIF system uses a pulse laser coupled with an optical detector to measure fluorescence via optical fibers. Measurements are made through a probe that is pushed into the ground with a truck-mounted CPT, widely used in the geotechnical industry for determining soil strength and soil type from measurements of tip resistance and sleeve friction. The LIF methods provide qualitative to semi-quantitative data on the *in situ* distribution of petroleum hydrocarbons from the fluorescence response induced in PNA compounds.

This report focuses on technology demonstration objectives in which the LIF sensor was evaluated as a field screening method by comparing, in particular, the downhole Nd:YAG SCAPS-LIF with the nitrogen-based SCAPS-LIF and to data produced by conventional sampling and analytical methods.

Generally, the SCAPS-LIF technologies produce results that agree well with conventional methods for qualitatively detecting subsurface petroleum. While the nitrogen-based LIF sensor has been certified by the California DTSC, the Nd:YAG SCAPS-LIF experienced difficulties in the field and has not gained formal regulatory acceptance. Nonetheless, as a field screening tool, SCAPS-LIF can delineate the distribution and boundaries of the contaminant source. At sites where the technology is applicable, results of the SCAPS-LIF field screening can be used to optimize the location and reduce the number of soil sampling borings and groundwater monitoring wells necessary to characterize a site. Such decisions can reduce the overall number of samples that need to be submitted for costly and time consuming offsite laboratory analyses, and the time and costs associated with multiple or iterative field investigations. A cost savings ranging from 30% to 50% is possible when compared with conventional screening methods.

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2.0 TECHNOLOGY DESCRIPTION

2.1 BACKGROUND

Site characterization currently represents a significant portion of remediation efforts, accounting for about one-third or more of total costs. Traditionally, environmental site characterization is based on drilling, sampling, and laboratory analysis. The problem is that subsurface contamination delineation is often based on trial-and-error placement of a significant number of monitoring wells and/or borings. Associated analysis is also time consuming and costly. Consequently, this site characterization approach has frequently hampered remediation efforts because of its uncertainty, cost, and time requirements.

SCAPS is a new, innovative technology which addresses many of these inefficiencies. SCAPS combines traditional CPT with real-time sensors to rapidly profile contaminants and geophysical properties in a cost-effective manner. This technology has been further developed through a collaborative effort of the Army, Navy, and Air Force under the Tri-Service SCAPS Program to include a fiber optic-based LIF sensor system for POL contaminants deployed via a standard 20-ton cone penetrometer.

2.2 THEORY OF OPERATION AND LIMITATIONS

The SCAPS-LIF technology represents a real-time, *in situ* field screening technique for characterizing the subsurface distribution of POL impact prior to the installation of monitoring wells or soil borings. As a field screening technique, it is not a replacement for soil sampling borings and monitoring wells; but is a means of reducing the number, and improving the placement, of boring and monitoring wells required for site characterization. It generates no solid wastes, such as drill cuttings, and only a minimal amount of waste water due to cleaning of the probe between push holes.

SCAPS-LIF obtains data by hydraulically pushing a small diameter, instrumented probe into the earth with a truck-mounted CPT. There is a laser-based instrument coupled to a window in the probe. Other sensors in the probe tip measure point penetration resistance and sleeve resistance of the geologic formation. These measurements are used to classify the soil. In addition, separate sample probes can obtain soil and fluid samples from selected locations. SCAPS is capable of obtaining a nearly continuous log of subsurface conditions, which is critical in determining the best remediation method.

The LIF sensor utilizes a fluorescence technique in which an optical response is stimulated in PNAs present in POL products. The SCAPS-LIF measures the fluorescence of PNAs in the contaminated soil matrix pressed against the surface of the probe's sapphire window. The LIF sensor accumulates the fluorescence signals induced by 20 consecutive laser pulses measuring discrete points along a small vertical interval of the subsurface. The system emits UV light that excites molecular electrons to excited/higher energy levels. As the electrons return to lower energy ground states, the transition produces UV and visible fluorescence photons of a longer wavelength than the UV excitation. Fluorescence stimulated in the *in situ* soil "sample" is detected through LIF sensors.

The fluorescence response is calibrated against a standard, either the same type of material as was released at the site (if known) or DFM, and site specific fluorescence and detection thresholds are determined.

Results from cone penetrometer pushes at the site are then compared to the fluorescence threshold to assess whether POL impact is present. Impact is considered to have been detected when the fluorescence signal intensity is greater than the site-specific threshold and the wavelength at which the maximum intensity occurs is similar to that of the standard. The SCAPS-LIF technology is limited to contaminants containing PNA compounds that fluoresce when exposed to 337 nm wavelength UV light; the most effective fluorescence response is obtained for POL products containing PNAs with three or more aromatic rings.

The sensor provides a nearly linear numerical response over a dynamic range of approximately three orders of magnitude starting from a minimum detection capability as low as 10's of ppm (weight of POL product/weight soil). However, the capability of this technology appears limited to a qualitative or semi-quantitative field screening method because sensor response has been shown to be very site specific, and vary as a function of soil type as well as the composition of the petroleum hydrocarbons being investigated. Limitations which may prevent an efficient site investigation using this technology, include:

- The SCAPS CPT support platform is a 20-ton Freightliner, all wheel drive, diesel-powered truck requiring a minimum access width of 10 feet and a height clearance of 15 feet. Some site areas may not be accessible to a vehicle of this size.

- Penetrometer limitations prevent use in hilly terrain and in some soils, such as conglomerate with cobbles and boulders or cemented materials. As with all intrusive site characterizations methods, it is extremely important that all underground utilities and structures be located before undertaking activities at a site.

- The relative response of the LIF sensor depends on the contaminant type and degree of weathering. The instrument's sensitivity to different hydrocarbon compounds can vary by as much as two orders of magnitude. This is primarily a reflection of the variations in the PNA distribution found within petroleum hydrocarbon products.

- The LIF sensor response to hydrocarbon compounds is also sensitive to soil matrix variations. Matrix properties that affect LIF sensitivity include soil grain size, mineralogy, moisture content, and surface area. Each of these factors influences the relative amount of analyte sorbed on or into the soil. Only the fraction of analyte optically accessible at the window of the probe contributes to the fluorescence signal.

- The LIF sensors will respond to any material that fluoresces when excited with UV. If present, non-POL fluorescent materials can interfere with system performance, providing false positive results or reduced sensitivity.

- The SCAPS-LIF technology is limited to sites where sufficient levels of PNA fluorophores exhibit significant fluorescent response at the 337 nm excitation wavelength which are above and distinguishable from background fluorescence levels. This technology has been shown to be applicable to a variety of sites contaminated by POLs, including DFM, diesel no. 2, JP-5, and unleaded gasoline. In its present configuration, the method cannot be used for direct detection of non-PNA (e.g., aliphatic or single-ring aromatic) compounds including BTEX compounds (e.g.,

benzene) or other compounds of concern that do not fluoresce at the 337 nm excitation wavelength.

2.3 SPECIFICATIONS

The SCAPS CPT system using a combination of reaction mass and hydraulics can advance a 1-m long by 3.57-cm diameter threaded-end rod into the ground at a rate of one meter per minute (in accordance with ASTM Standard D3441). Data acquisition is automated under software control using a host computer. The computer controls the sensor system, stores fluorescent emission spectra and strain gauge data, and generates the real-time depth plots shown in Figure 1. From the spectra emission curve at each depth, the SCAPS software extracts the maximum intensity and associated peak wavelength for real-time depth display. The standard cone penetrometer instrumentation consists of strain gauges measuring tip resistance and sleeve friction in accordance with ASTM Standard D3441. This data is contained in real-time display strips as Cone Pressure, Sleeve Friction, and Soil Classification (see Figure 1). Additional specifications are discussed below.

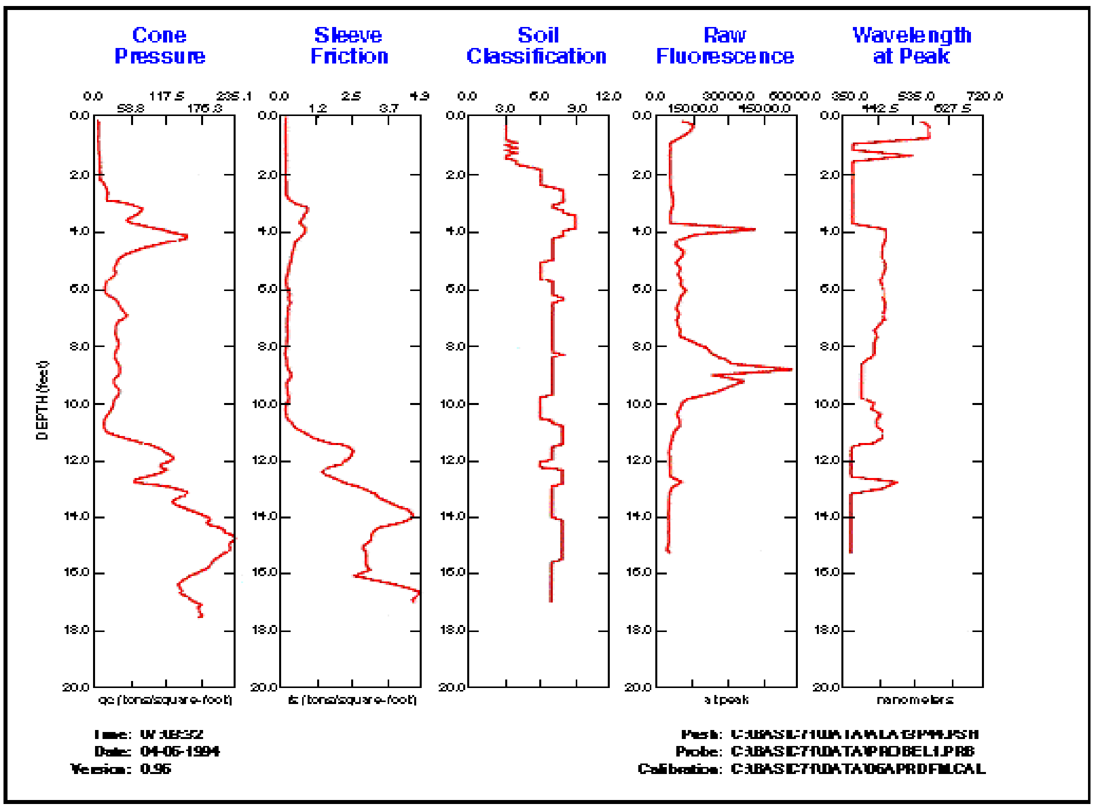

Figure 1. Real-Time Data Display of Fluorescence and Strain Gauge Data

- **Cone Penetromenter LIF Probes.** The SCAPS-LIF system use a steel probe containing the LIF sapphire optical window and cone and sleeve strain gauges. The excitation and emission optical fibers are isolated from the soil system by a 6.35 mm diameter sapphire

window located 60 cm from the probe tip, mounted flush with the outside of the probe. The SCAPS-LIF fibers are 365 mm in diameter and up to 100 m in length.

- **Laser Sources.** The SCAPS-LIF system currently has been used with three different laser sources: nitrogen, excimer (xenon chloride), and Nd:YAG (Neodymium:Yttrium Aluminum Garnet). The original system was developed using a 337 nm nitrogen-based laser. The 266 nm Nd:YAG laser represents a modification of the nitrogen-based system and is more effective at detecting single ring aromatics. The excimer system emits a 308 nm laser. Figure 2 illustrates a schematic of a Nd:YAG system.

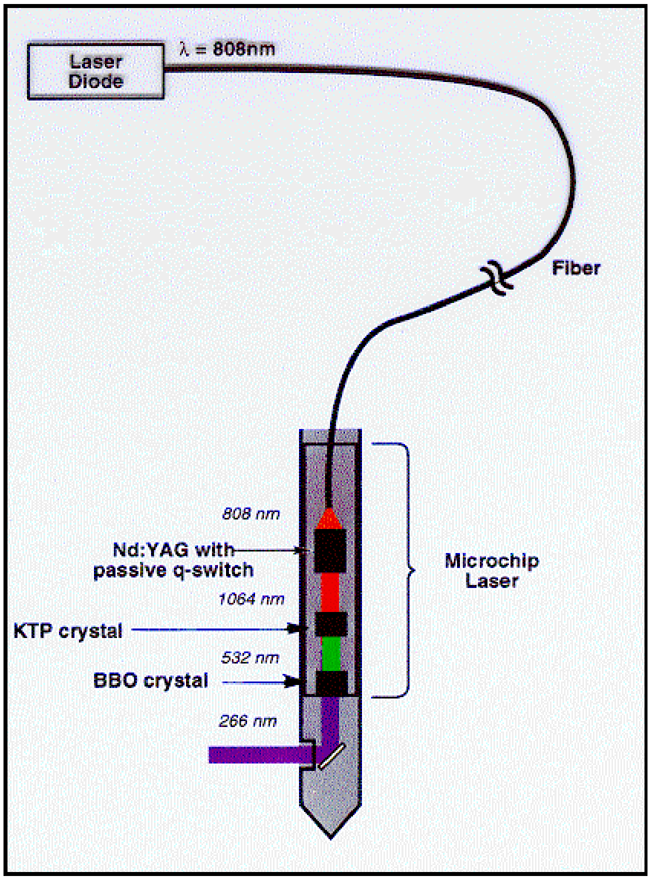

Figure 2. Schematic of Nd:YAG Laser System

- **Detection System.** The SCAPS-LIF system detects fluorescence with a fiber optic-based sensor. As the pulse from the laser is launched into the excitation fiber, a photodiode is triggered which generates a synchronization pulse that is fed into a pulse delay generator. This pulse is used to gate on a PDA detector. Fluorescence stimulated in the *in situ* soil "sample" by the laser is collected by the emission fiber and returned to a spectrograph, where it is dispersed spectrally on the PDA. For a laser firing at a rate of 20 Hz, an entire fluorescence emission spectrum measurement, composed of a 20 laser shot average, can be collected in approximately one second.

Under normal operating conditions, fluorescence emission spectra are collected once per second as the penetrometer probe is pushed into the ground at a rate of approximately 1 m/min. This yields a measurement with a vertical spatial resolution of about 0.2 feet. The host computer equipped with custom software controls the fiber optic fluorometer sensor system and stores fluorescence emission spectra and conventional CPT sleeve friction and tip resistance data. The host computer generates real-time depth plots of fluorescent intensity at the spectral peak, wavelength of spectral peak, sleeve friction and tip resistance, and soil type characteristics as interpreted from strain gauge data. The entire fluorescence emission spectrum is stored on a fixed hard disk to facilitate post-processing of the data.

- **Noise, Background, and Sensitivity.** Three levels of measurement are needed to obtain the fluorescence threshold and detection limit: noise, background, and sensitivity. These levels of measurement are determined via calibration samples prepared immediately prior to the site visit using soil from the site and standard analytical techniques. The fluorescence intensity for each calibration sample is measured in triplicate daily at the start of operations and averaged to provide a single measured intensity. The data is statistically regressed whereby the intercept is the intensity of the unspiked calibration standard (0 ppm) and the slope is determined by the least squares fit method. The noise is defined as 1.00 times the standard deviation in order to establish a conservative fluorescence threshold. Using the standard assumption of a normal "student's t" distribution, and the number of points used in these fits (typically four to five points), this corresponds to an 80% confidence limit.

- **Fluorescence Threshold and Detection Threshold.** Once the noise, sensitivity, and background levels are established, the fluorescence threshold and the detection can be determined. The fluorescence threshold (i.e., the quantitative limit that the fluorescence intensity must exceed in order to qualify as a "detect.") is equivalent to the background plus the noise. The detection threshold (i.e., the practical detection level of contaminant that corresponds to the fluorescence threshold) equals the noise divided by the sensitivity (which is the standard deviation of the fit over the slope of the fitted data). Based on the results calculated from the nitrogen-based SCAPS- LIF system, the detection threshold will vary from about 100 to 300 mg/kg.

2.4 MOBILIZATION AND OPERATIONAL REQUIREMENTS

Typically, a four person crew is needed to complete field operations including one field geologist, two push room personnel, and one LIF system operator. CPT operation encompasses a large part of the field activities; the responsibilities and training are similar to those of standard geotechnical CPT. The LIF system operator requires a background in science and more detailed system component training in order to diagnose and correct field equipment problems. The SCAPS truck-mounted CPT platform is a stand-alone operations unit requiring neither outside utilities nor special structures (either permanent or temporary). The CPT platform provides a 20-ton static reaction force associated with the weight of the truck. A generator supplies all power operated off the truck diesel motor and regulated through an uninterruptable power supply with a battery bank. A truck-integrated hydraulic system advances the rods and the chemical and geotechnical sensing probe, and powers the grout pump. As the rods are withdrawn, grout can be injected through umbilical interior tubing, hydraulically sealing the push hole. The SCAPS does

not bring significant quantities of soil to the surface; however, IDW will be generated during the steam cleaning of the rods and probes during retraction. The forward portion of the truck-mounted laboratory is the push room. The push room contains the rods, hydraulic rams, and associated system controllers. Underneath the push room is the steam cleaning manifold for the rod and probe decontamination system. The rear portion of the truck-mounted laboratory is the isolatable data collection room in which components of the LIF system and onboard computers are located. Water from onboard tanks is consumed by the steam cleaning system and during grouting. A local source of water is required for refilling the onboard tanks. Other consumables are grout and high purity nitrogen gas for the laser.

2.5 COMPARATIVE ADVANTAGES AND STRENGTHS

The SCAPS-LIF systems were developed to provide real-time *in situ* measurements of both subsurface contamination and geophysical properties at hazardous waste sites. The method is not intended as a complete replacement for traditional soil borings and monitoring wells. Instead, the LIF sensors are *in situ* field screening techniques for qualitatively characterizing the subsurface distribution of POL impact prior to the installation of groundwater monitor wells or soil borings. Subsequently, the site can be further characterized with limited numbers of carefully placed stab samplings, borings, or wells. In addition, remediation efforts can be expedited based on the immediate availability of the LIF and soil matrix data. In addition, the SCAPS CPT platform allows for the relative characterization of contaminated sites with minimal exposure of site personnel and the community to toxic contaminants, and minimizes the volume of IDW.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The overall goal of the SCAPS-LIF technology is to provide semi-quantitative data on the *in situ* distribution of POL products based on the fluorescence response induced in their PNA component compounds. Key performance objectives included the following:

1. Detailed, near continuous measurements that map subsurface POL distribution,
2. Agreement of the LIF POL impact distribution with analytical measurements,
3. Agreement with data collected using a conventional CPT stab soil sampler (accepted nitrogen systems meet or exceed 80%),
4. Collection and storage of the entire fluorescent spectrum from the push,
5. Distinction between hydrocarbon classes as well as discriminate non-hydrocarbon fluorophores present in the soil,
6. Real time acquisition of data as the sensor is advanced into the ground,
7. Detection of the presence of hydrocarbons in the bulk soil matrix throughout the vadose, capillary fringe, and saturated zones,
8. Measurements of up to depths of 150 feet,
9. Provision of continuous geotechnical and stratigraphic information (e.g. cone pressure and sleeve friction),
10. Minimize the possibility for contaminating or altering soil samples,
11. Accurate contamination depth measurements,
12. Production of a minimal amount of IDW.

3.2 PHYSICAL SETUP AND OPERATION

The SCAPS-LIF system was setup and operated as described in Section I-D: Mobilization and Operational Requirements. Steam cleaning rinsate water was collected in DOT-rated 208 liter (55 gallon) drums and handled as potentially hazardous waste. Operations yielded approximately half a drum of rinsate waste per day. Wastewater disposal was coordinated with the site's responsible party and handled locally after analysis results were obtained. Predemonstration investigation activities required approximately ten

field days for each site. Sampling activities required one or two field days at each site (site locations are identified in Section II-E: Demonstration Site/Facility Background section).

3.3 SAMPLING PROCEDURES

To verify the data, the conventional CPT stab sampling method was tested along with the SCAPS-LIF technology. Testing at each site had slightly different sampling procedures. In general, the SCAPS CPT pushed the LIF probe into the selected location and acquired the corresponding data. The CPT stab sampling advanced the probe into the push hole using 6.6-inch long, 1.5-inch diameter, hollow stainless steel tubes. In the cases where multiple LIF technologies were demonstrated, each following push location was moved approximately 20 cm from the previous. Soil samples were collected at depths where the LIF technology indicated the presence of hydrocarbons. Only samples that were relatively undisturbed were used. Each sample was sealed and stored in containers maintained at a constant temperature (about 4EC) with ice, and then shipped to the designated laboratory in the stainless steel tubes retrieved from the sampler.

3.4 ANALYTICAL PROCEDURES

The confirmatory analytical methods chosen for the SCAPS-LIF technology were the DHS Method 8015-Modified for TPH and EPA Method 8021A-Modified for BTEX and MTBE. These methods were selected due to their widespread and generally accepted use in delineating the extent of petroleum hydrocarbon contamination. The DHS method determines aromatic hydrocarbons in the C6 to C40 range. The DHS method utilizes a gas chromatograph coupled with a flame ionization detector to separate the components by molecular weight. The chromatogram produced by this analysis covers the range from C7 to C36 and can assist in identifying the product type. The EPA method employs a purge and trap technique in which an inert gas is bubbled through either the contaminant extract of the soil or the contaminated water sample. Then the volatiles are passed through a gas chromatograph with a photoionization detector and an electrolytic conductivity detector. The measurement of this volatilized sample is compared to similar measurements of standard solutions containing BTEXs and MTBE as well as soil samples spiked with BTEX and MTBE standards, in order to quantify the contaminants.

3.5 DEMONSTRATION SITE/FACILITY BACKGROUND

The objective of the SCAPS-LIF demonstrations was to generate site specific field data appropriate for verifying the field screening performance of the technology, and thereby facilitate the technology's acceptance and use by the representative regulator and user communities. The potential sites were selected based on the following criteria:

- availability of the sites for the demonstration;
- accessibility to two-wheel drive vehicles;
- soil impacted by petroleum hydrocarbons, containing mixtures of single and multiple ring aromatic compounds;

- soil types consisting of unconsolidated sediments of native sands, silts, clays and gravel which are suitable for CPT pushing;
- previous analytical results indicating adequate levels of petroleum contamination to demonstrate the SCAPS LIF technology.

Figure 3. Photograph of NAS North Island Site with Push Locations Marked with Cones

3.6 DEMONSTRATION SITE/FACILITY CHARACTERISTICS

The SCAPS-LIF technology was developed to perform rapid field screening to determine the presence of POL subsurface impact. To test this capability, sites were identified that were considered conducive to the application of this technology, yet, exhibited a range of physical and chemical characteristic, including:

- Continental, coastal, and marine-type deposits comprised of sandstone, sands, silts, gravel, and clays. To note, POL impact in sand matrices generally has a higher fluorescent response than that found in finer-grained matrices.

- Groundwater present at depths from approximately 6 to 500 feet below ground surface, yet, not precluding the presence of perched water tables.

- The existence of selected POL compounds, including JP-5 and DFM, present in the vadose zone as LNAPL.

- "Simple" sites marked by homogeneous, shallow subsurface conditions and impact and "complex" sites marked by varying stratigraphy and deeper, varying contaminant concentrations.

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4.0 PERFORMANCE ASSESSMENT

4.1 FIELD DEMONSTRATIONS

A number of SCAPS-LIF field demonstrations have been completed. A summary of NRaD field demonstrations is provided in Appendix D. Additional selected, expanded field demonstration summaries are provided below.

- **Port Hueneme, California (April - May 1995).** This demonstration involved testing of the nitrogen laser SCAPS-LIF system in a DFM impacted area. A total of 15 SCAPS-LIF pushes were completed along with 15 co-located confirmation sample borings from which 232 samples were collected and analyzed for both TRPH and TPH. The site detection limit and fluorescence threshold were 109 mg/kg DFM, and 3,558 counts, respectively. For the 232 TPH analyses completed there were 29 (12.5%) true positives, 190 (82.2%) true negatives, 4 (1.7%) false positives, and 9 (3.9%) false negatives. For the 232 TRPH analyses completed there were 28 (12.1) true positives, 189 (81%) true negatives, 5 (2.2%) false positives, and 10 (4.3%) false negatives. Demonstration results are illustrated in Appendix E. The fluorescence response pattern with depth data for each push location was compared with the results of the co-located boring confirmation samples. With this approach there was only one apparent anomaly, as the vertical pattern of contamination determined via the nitrogen laser SCAPS-LIF technology for each borehole generally matched that determined by the traditional method of core sample analysis.

- **Albuquerque, New Mexico (November, 1995).** This demonstration involved testing of the nitrogen laser SCAPS-LIF system at a Sandia National Laboratories fuel tank farm site impacted by diesel fuel No. 2. Previous excavation had been conducted at this area; however, it was not clear whether the excavation was filled with only the contaminated soil that was removed or with other offsite fill material. During the SCAPS-LIF pushes, significant background fluorescence was observed, primarily due to calcium carbonates (HCL addition to soil cores resulted in the release of carbon dioxide). In addition, significantly higher fluorescence responses due to carbonates occurred in the fill zone. It was also noted that the fluorescence characteristics of the shallow soil sample used to prepare the calibration samples were not representative of deeper soils below the fill. 3 CPT pushes along with 3 co-located borings from which 92 confirmation samples were obtained for TPH and TRPH analysis. The data were reviewed based on the lower site detection and fluorescence threshold values determined for the site, 88 mg/kg DFM, and 1,094 counts, respectively. For the 92 TPH analyses completed there, were 68 (74%) true positives, 7 (8%) true negatives, 17 (18%) false positives, and 0 (0%) false negatives; identical results were obtained using TRPH data. A higher number of false positives (14 of 17) occurred primarily above the 14 foot depth within the fill material. Demonstration results are illustrated in Appendix F. Removing these samples corresponding to the background emission spectra gave overall results consistent with the results achieved in the April - May 1995 Port Hueneme demonstration.

- **North Island Fuel Farm at NAS San Diego, California (November, 1996).** Three sets of co-located investigations; SCAPS downhole Nd:YAG LIF push, SCAPS nitrogen LIF push and the Mostap stab sampler CPT push were advanced during validation operations at a leaking

underground tank area impacted by both dissolved and free phase JP-5 and DFM. 37 discrete soil samples were collected and analyzed by traditional methods as part of the validation effort. In general, comparisons of nitrogen and downhole Nd:YAG LIF data correlate well. Discrepancies occur at the plume edges where the presence of the contaminant changes rapidly with slight changes in depth. One nitrogen LIF push which exhibited background fluorescence response, showed TPH values of less than 25 mg/kg, while another nitrogen LIF push exhibited elevated fluorescence and TPH concentrations as high as 130,000 mg/kg.

- **NEX Service Station at NCBC Port Hueneme, California (March, 1997).** Validation field operations were conducted at an active petroleum dispensing facility having documented releases of gasoline into the subsurface. 6 SCAPS nitrogen laser LIF pushes, 6 downhole Nd:YAG LIF pushes, and 14 SCAPS CPT stab sample pushes were completed along with 8 SCAPS xenon chloride LIF pushes. A total of 23 soil samples were collected. 6 investigative points consisted of a SCAPS nitrogen LIF push, a SCAPS xenon chloride LIF push, a SCAPS downhole Nd:YAG LIF push, and a SCAPS soil sample push. Some difficulties were experienced involving the probe depth. The SCAPS software had the distance from the probe tip to the sapphire window set so it could not be altered. However, all three LIF probe window locations were different from that in the software. The nitrogen and excimer LIF probes' actual window position was 0.5 feet further from the probe tip, while the downhole Nd:YAG LIF probe's actual window depth was 0.2 feet closer to the probe tip. Thus, the recorded and actual probe depths are not the same. Also, the strain gauges did not function properly in the downhole Nd:YAG LIF probe and soil classification profiles could not be gathered during those pushes. This data was collected during the nitrogen and excimer laser pushes.

- **Other Studies.** The nitrogen-based SCAPS-LIF certification evaluation also included demonstrations at Naval Air Weapons Station China Lake, and Marine Corps Air Ground Control Combat Center Twentynine Palms. These efforts provided valuable first-hand information on how the system and its operators perform when the technology is deployed at a site where little or no subsurface information is available. It was also important to understand how the system is routinely calibrated and operated, what difficulties different site conditions might present, and how operations can be adjusted accordingly.

4.2 FIELD DEMONSTRATION RESULTS

The demonstration results showed that all three laser systems (SCAPS nitrogen, SCAPS excimer, and SCAPS downhole Nd:YAG) yielded very similar patterns of subsurface contamination. Qualitatively, *in situ* measurements compare favorably with laboratory measurements of validation soil samples. Furthermore, given the effectiveness of the 266 nm laser source for inducing fluorescence in the single ring aromatic compounds, the Nd:YAG laser system demonstrated the capability to directly detect spectral differences in emission signatures at plume boundaries. However, several field performance deviations were noted, including the following:

- The downhole Nd:YAG laser experienced instability in the output thought to be a result of thermal variations induced by frictional forces as the probe is pushed into the ground. Other thermal

variations resulted from the steam cleaning procedure that is normally used to clean the CPT probe upon withdrawal from the push hole. Even when the steam cleaning procedure was modified to minimize heating of the probe section, unacceptable high variability in laser output was still experienced.

- Due to the nature of the conventional subsurface sampling process used for verification, there was some variability in the data and sample depth. Because of a concern about the loss of volatiles, soil samples for the Nd:YAG testing were not homogenized prior to evaluation for TPH. As a result, these soil samples were collected at a depth slightly offset from the *in situ* data. This difference is not as important in the heavily contaminated regions of the plume, but it may affect correlations in regions with marked gradient conditions (e.g., the upper and lower portions of the plume as well as the leading edge).

4.3 TECHNOLOGY COMPARISON

The SCAPS-LIF method provides real-time data as the probe is pushed into the ground enabling timely field modifications to the sampling plan. This capability provides a more thorough investigation and avoids the drawn out iterative process typical of site characterization when using traditional sampling and off-site laboratory analysis.

The validation effort has produced comparison data to support the utility of SCAPS-LIF application. In general, comparisons of laboratory 8015 modified (TPH), 8021A modified, and 8260 results versus fluorescence show that laboratory results track patterns observed for *in situ* fluorescence data well.

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5.0 COST ASSESSMENT

5.1 COST PERFORMANCE

Factors affecting the cost of SCAPS-LIF operations include labor, material, travel, permitting, utility location, location surveying, work plan and report preparation, and equipment mobilization. Additional cost may be incurred if the ground surface is too hard for penetration (e.g., cement or asphalt). The SCAPS-LIF cost has been quoted as $4,000 per day plus per diem.

5.2 COST COMPARISON

As with any analytical instrument, the cost for a site investigation is dependent upon the number of samples analyzed. For the SCAPS-LIF technology, this is equivalent to the number of data points collected, which by itself is a function of the number of pushes and the depth per push. Depth resolution of data points is approximately 1 to 2 inches. Therefore, the major determinant of the cost of characterizing a site is the size of the area under investigation. In a field screening scenario, Table 1 presents a comparison between the costs using SCAPS-LIF versus conventional drilling (e.g., using both hollow stem auger/split spoon and direct push technology), sampling, and laboratory analysis for a site with 10 holes to a depth of 30 feet. The table shows the cost for SCAPS-LIF is approximately one third the cost of conventional sampling. On a per sample basis, the conventional sampling is approximately 100 times more costly. For the SCAPS-LIF technique, regulators may require a minimum number of confirmatory samples, which can be obtained using CPT sampling devices. This would increase the SCAPS-LIF cost as presented in the table but only three or four samples would be required at less than $1,000 additional cost.

Table 1. Cost Comparison of SCAPS CPT/LIF and Conventional Sampling

SCAPS-LIF *In situ* Measurement[1]		Conventional Drilling (hollow stem auger, split spoon, and offsite analyses)[1]		Direct Push and Offsite Analysis[2]	
10 Pushes to 30 ft.	Cost	**10 Borings to 30 ft. (60 soil samples for TPH analysis)**	Cost	**10 Borings to 30 ft. (60 soil samples for TPH analysis)**	Cost
2 Field Days @ $4,000/day	$8,000	Drilling for 300 ft. @ $50/ft	$15,000	Drilling for 300 ft. @ $10/ft	$3,000
1 sample/2 inches (1,800 total samples)	Included in Cost	TPH Analysis for 60 samples @ $80/sample	$4,800	TPH Analysis for 60 samples @- $80/sample	4,800
Geotechnical Data for 1 sample/inch	Included in Cost	Geotechnical Analysis for 5 samples @ $100/sample	$500	Geotechnical Analysis for 5 samples @ $100/sample	$500
4 Waste Drums @ $40/drum	$160	28 Waste Drums @ $40/drum	$1,120	1 Waste Drum @ $40/drum	$40
Decon Water Testing	$1,000	Decon Water Testing	$1,000	Decon Water Testing	$1,000
Waste Soil Testing	$0	Waste Soil Testing	$3,000	Waste Soil Testing	$0
Waste Soil Disposal	$0 (none produced)	Waste Soil Disposal for 20 Drums @ $100/drum	$2,000	Waste Soil Disposal	$0 (none produced)
Decon Water Disposal for 4 Drums @ $100/drum	$400	Decon Water Disposal for 4 Drums @ $100/drum	$800	Decon Water Disposal for 1 Drum @ $100/drum	$100
4 Man Crew	Included in Cost	Geologist for 40 hours @ $60/hr	$2,400	Geologist for 24 hours @ $60/hour	$1,440
		Technician for 40 hours @ $40/hr	$1,600		
TOTAL	**$9,560**	**TOTAL**	**$32,220**	**TOTAL**	**$10,880**
Per Sample Cost for 1,800 samples	$5.31	Per Sample Cost for 60 samples	$537	Per Sample Cost for 60 samples	$181

1 - ESTCP Technology Demonstration Report, December 1997

2 - Personal Communication, TerraProbe, May 10, 1999

Several case studies are discussed below:

- A Los Alamos report, "Cost Effectiveness of the Site Characterization and Analysis Penetrometer System" focused on SCAPS-LIF effectiveness to improve the placement and reduce the number of monitoring wells. For a set of scenarios, cost was compared between site characterization (e.g., drilling, coring, and installing monitoring wells) with and without using SCAPS-LIF. It was concluded that a cost savings of 30% to 50% over the use of conventional methods is possible assuming 50% of planned wells can be avoided by the use of SCAPS.

- At the 4.5 acre Navy Fleet Industrial Supply Center, Manchester site, a SCAPS study was Determined to cost $110k versus $188k for the traditional study; a savings of approximately 40%. These values represent total project costs including plans, reports, and field work. SCAPS was also deemed a more complete characterization due to its real-time, high-resolution data; however, neither this advantage nor the time and cost savings with minimizing return site visits were quantified in the analysis.

- The Army Corps of Engineers Savannah District used SCAPS-LIF, whereby, impact was detected 30 to 40 feet below the water table - impact that conventional sampling methods would have been expected to miss. The installation saved $100k by eliminating 25 wells, and $50k in sampling costs. The team also characterized the site in 8 weeks; the process could have taken 14 weeks using conventional methods.

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6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

The range of anticipated saving that may be achieved at any given site is highly variable; however, site savings should be expected to vary from 0% to 30% of the total field investigation cost. Large sites with complex geology are expected to show the greatest savings, while small sites are expected to yield little or no savings. The majority of the costs for the SCAPS-LIF method are fixed, amounting to $4,000 per day and include all equipment and manpower. Conditions which might increase total cost include asphalt removal, travel, permitting, and surveying.

6.2 PERFORMANCE OBSERVATIONS

There were noticeable performance differences between bench- and pilot-scale testing. For example, problems with variable laser output, which appear to be temperature related are much more severe in the field than in the laboratory. In addition, comparison between *in situ* measurements and those from laboratory analyses of discrete samples proved problematic due to subsurface heterogeneity. These sampling problems are further exacerbated with sample integrity concerns that preclude compositing and homogenization of samples.

In addition, a better method needs to be implemented for controlling the power output of the Nd:YAG laser system. It should be noted that the Nd:YAG laser system used in the demonstrations was a prototype system and that the technology has undergone improvements. Also, the UV passively Q-switched microchip lasers have been licensed to Uniphase Lasers and Fiberoptics with the intent of being commercially available by 1999. It is likely the commercialized product may be more stable and better able to accommodate variations in environmental conditions.

6.3 OTHER SIGNIFICANT OBSERVATIONS

There is a semi-quantitative aspect to this technology; order of magnitude changes in fluorescence response at the contaminant's response wavelength generally indicate real changes in contaminant concentrations. Method sensitivity and detection limits are very site specific and depend on both the subsurface lithology and contaminant composition. Determining applicability of the technology requires system calibration with representative soil samples from the site spiked with varying concentration of a specific POL constituent or other standard, as well as traditional confirmation boring sample analyses.

Fluorescence-based direct push sensors are currently being marketed in the United States and Europe by at least four different primary suppliers. In addition, there are presently nine systems being operated by the U.S. Government (4 Army, 3 Navy, 1 DOE, and 1 US EPA). Implementation of a mature configuration of the newer Nd:YAG system is commercially very attractive because it makes use of a simple solid-state device (compared to present laser sources) that provides a capability that meets or exceeds that of present commercial systems.

6.4 REGULATORY AND OTHER ISSUES

The SCAPS-LIF technology has achieved certification (i.e., nitrogen-based LIF system) to provide qualitative screening level data for the determination of POL impact in soils (see Appendix G). Furthermore, the SCAPS-LIF system is currently being either evaluated or demonstrated by several technology certification programs, including the ITRC, Cal-EPA - Technology Certification Program, U.S. EPA, Department of Defense, and Department of Energy - Consortium for Site Characterization Technology, and Western Governor's Association - Committee to Develop On-Site Innovative Technologies.

DTSC has indicated that certification of the SCAPS-LIF is subject to a various specific conditions, including: (1) Site Applicability; (2) Calibration; (3) Confirmation Borings; (4) Spectral Response Data Interpretation; (5) Grouting; (6) Probe Cleaning; (7) Continuous Quality Control/Quality Assurance; (8) Modifications and Amendments at the Request of the Applicant; (9) Requirements and Conditions of New Regulations; and, (10) Maintaining Product Quality and Monitoring by DTSC. This certification is likely to facilitate and encourage the acceptance of this technology as a field screening method for site characterization in other regulatory settings.

6.5 LESSONS LEARNED

The SCAPS-LIF system has application as field screening technology at sites where the contaminant source is from POL products or wastes containing PNAs, such as diesel fuel, JP-2, DFM, bunker fuel, crude oil, refinery wastes, or unleaded gasoline; in addition, there may be potential application for MGP sites. The site lithology must be applicable for CPT penetration. SCAPS-LIF is intended to delineate the horizontal and vertical boundaries as well as the three-dimensional distribution of the subsurface contaminant source; at this time, it is not intended to identify dilute dissolved-phase contaminant plumes. Use of the technology is limited to POL impacted sites where sufficient levels of PNA fluorophores are present in the hydrocarbon matrix to exhibit significant flourescent response at the 337 nm excitation wavelength which are above and distinguishable from background fluorescent levels. If strong naturally occurring fluorophores are present, it must be determined whether these may interfere with the technology's effectiveness.

The SCAPS-LIF system can provide relatively rapid, vertically continuous, real-time, *in situ* analysis for the detection of subsurface POL impact both above and below the water table. It can be used for field screening at sites with no historic subsurface characterization data, or to further delineate the contamination at sites where some level of conventional characterization work has been completed. Where applicable, results of the SCAPS-LIF field screening can be used to optimize the location and reduce the number of soil sampling borings and groundwater monitoring wells necessary to characterize a site. Such decisions can reduce the overall number of samples that need to be submitted for costly and time consuming offsite laboratory analyses, and the time and costs associated with multiple or iterative field investigations.

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APPENDIX A

Points of Contact

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APPENDIX B

SUMMARY OF NRaD FIELD VALIDATION STUDY RESULTS

SITE	Lithology	Water Table (ft. bgs.)	Reported Contamination	Calibration Std.	Detection Threshold (mg/kg)	Fluorescence Threshold (counts)	Sensitivity (counts / mg/kg)	# Pushes	Max. Push Depth (ft.)	# borings	# confirm. samples	TPH (1) TRPH true +	true -	false +	false -
Alameda NAS	Sand, Silty Sand, Silty Clay	5	Refinery Waste, JP-5, Gasoline	DFM	137	10820	5.62	45	22	8	46	16 19	23 22	4 1	2 3
San Diego NTC	Sand, Silty Sand, Clay	6	Waste Motor Oil	No. 2 Diesel	1141	1064	0.22	18	19	4	18	9 10	8 8	2 1	0 0
U. S. Marine Corp. Air Station, Yuma - Fire School Area	Fine Sand, Silt, Clay (CaCO3 within Clays)	-	JP-5, diesel, gasoline	DFM	888	1358	0.74	29	72	4	23	1 1	19 19	1 1	2 2
San Diego NAS Fire Fighter Tolning Facility	Fill (gravels, sands, silty sand, clayey sands)	10	JP-5	DFM	466	108	0.2	22	16	3	12	5 5	4 4	1 1	2 2
Unocal Guadalupe Oil Field	sands/silty sands	79	diluent (kerosene-like)	diluent	90 visual	300 visual	0.55 *	24	101	4	16	7 6	7 8	1 2	1 0
Coronado, Naval Amphibious Base Abandoned Fuel Farm Site	fine medium sands (trace gravels)	-	diesel, gasoline	DFM	285	19953	4.07	22	15	3	9	3 3	6 6	0 0	0 0
Camp Pendleton Marine Corp. Air Station - Area 23 Ground Control Approach Facility Site	silty sand	4	diesel	DFM	745	2134	1.12	25	23	4	14	0 0	14 14	0 0	0 0
San Diego, NASNI Underground Storage Tank Site	sands, interbedded gravel	24	diesel	DFM	286	6127	1.2 0.4 (3)	25	31	4	26	0 0	21 17	0 0	5 9
Naval Training Center San Diego (2) NEX Service Station	clays fine sands	12	unleaded gasoline	DFM	1051	811	0.2	33	26	4	24	nd nd	nd nd	nd nd	nd nd

	# confirm. samples	true +	true -	false +	false -	TOTAL
TPH		41	102	9	12	164
%		25.0%	62.2%	5.5%	7.3%	100.0%
TRPH		44	98	6	16	164
%		26.8%	59.8%	3.7%	9.8%	100.0%
TOTAL	188	85	200	15	28	328
% False				4.6%	8.5%	13.1%

Notes:
1) true + = true positive
true - = true negative
false + = false positive
false - = false negative
2) calibration procedure performed approx. 5 months after field operations using different probe
3) reduced sensitivity of local contaminant vs. DFM

* estimated
nd not determined

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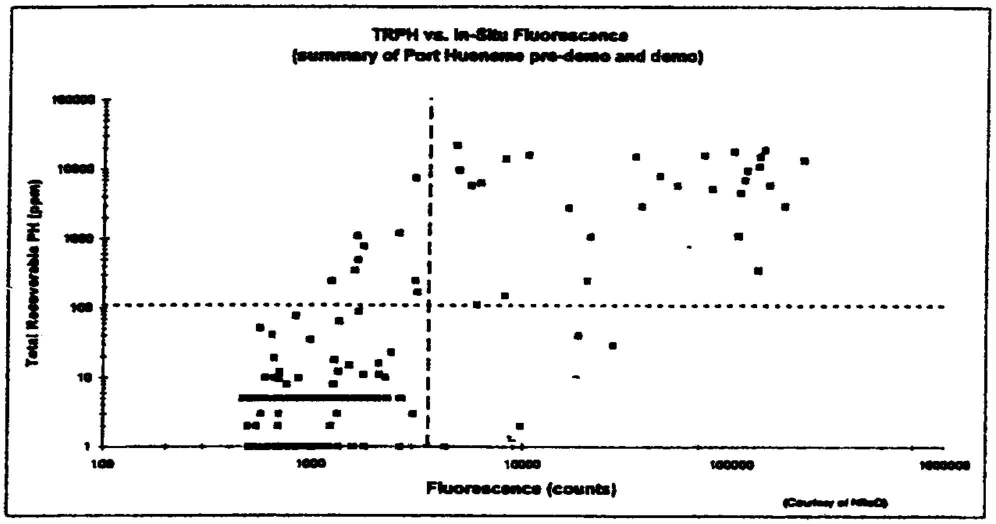
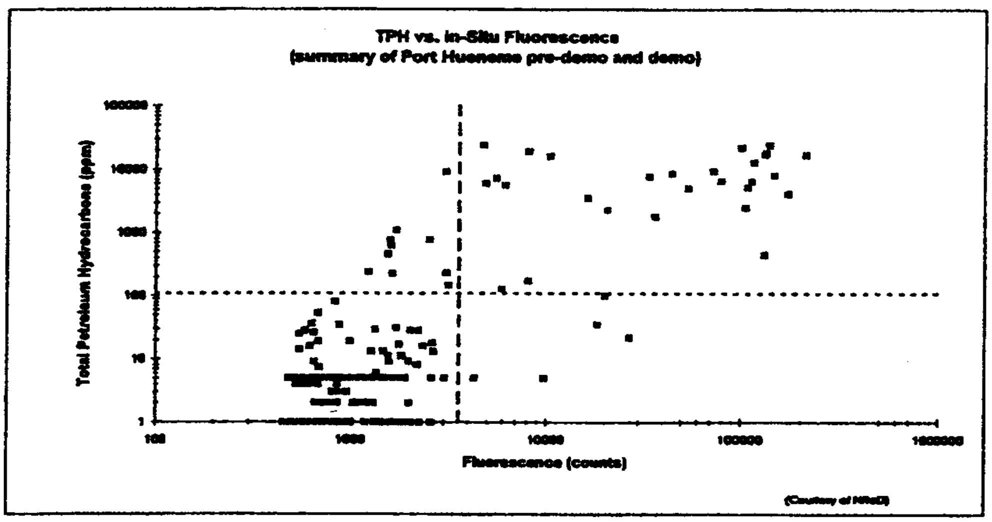
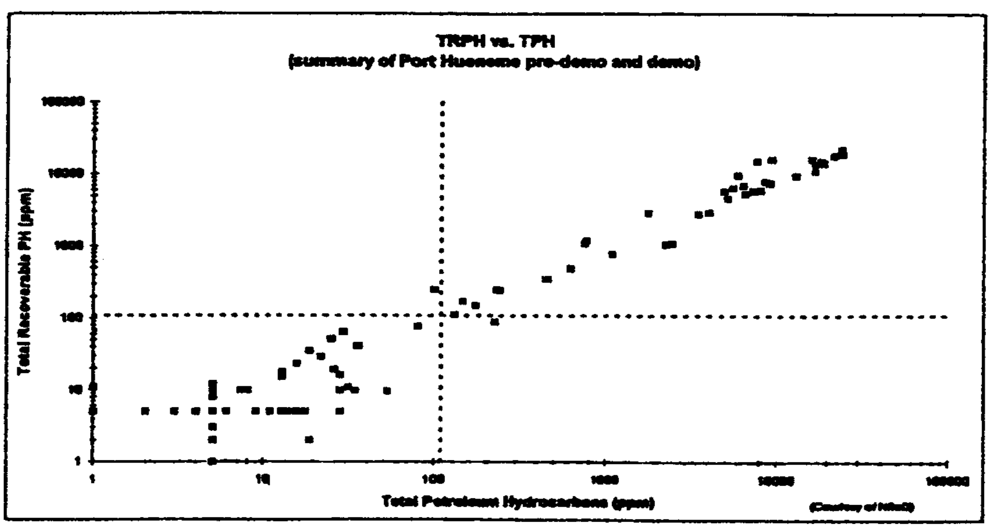
APPENDIX C

Port Hueneme Demonstration

ATI Laboratory and In-Situ Fluorescence Results







- - - - - - Detection Limit, 109 mg/kg DFM (average of Port Hueneme demonstration and pre-demonstration calibration results)

— — — — Fluorescence threshold, 3656 counts (average of Port Hueneme demonstration and pre-demonstration calibration results)

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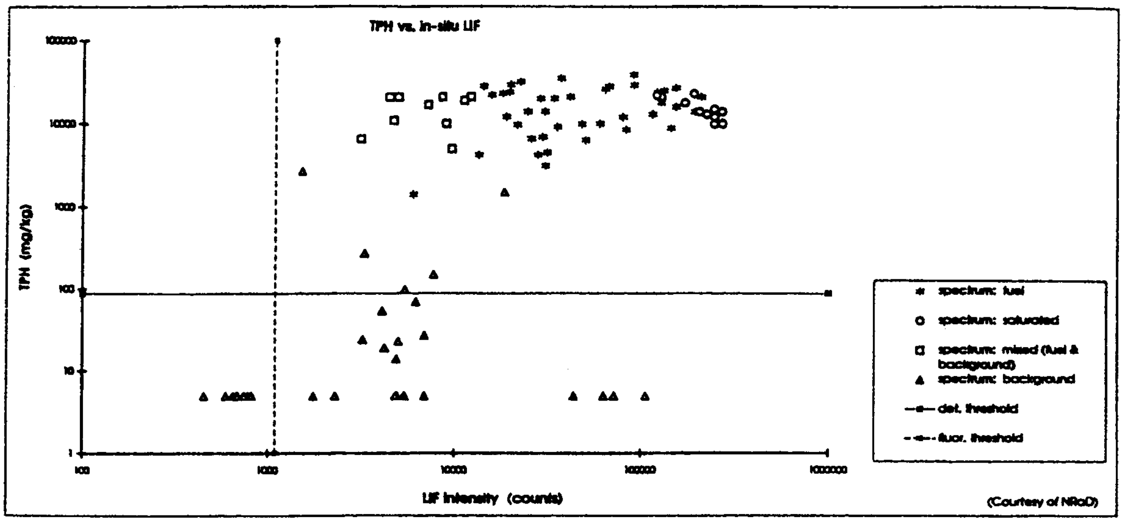
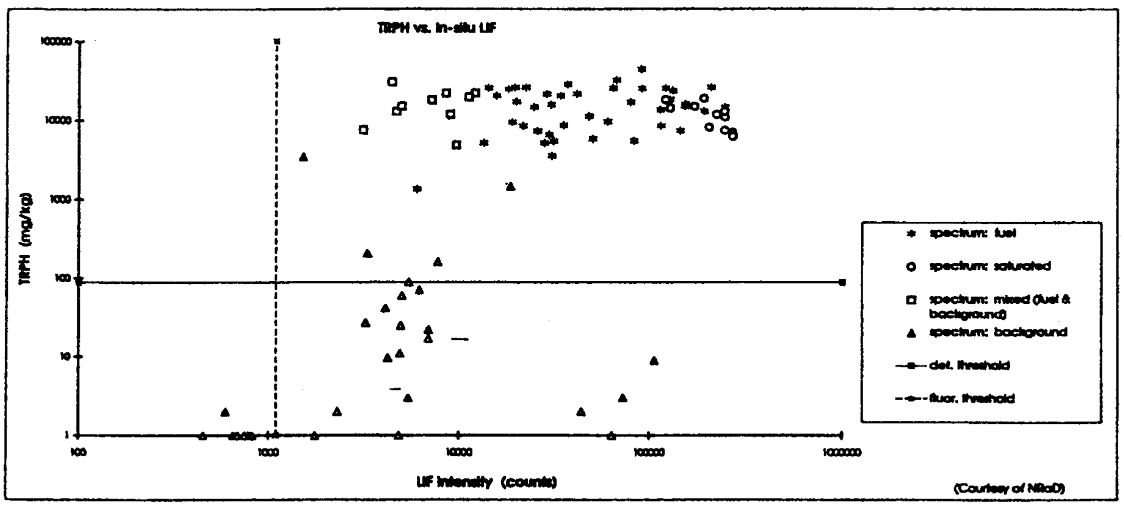
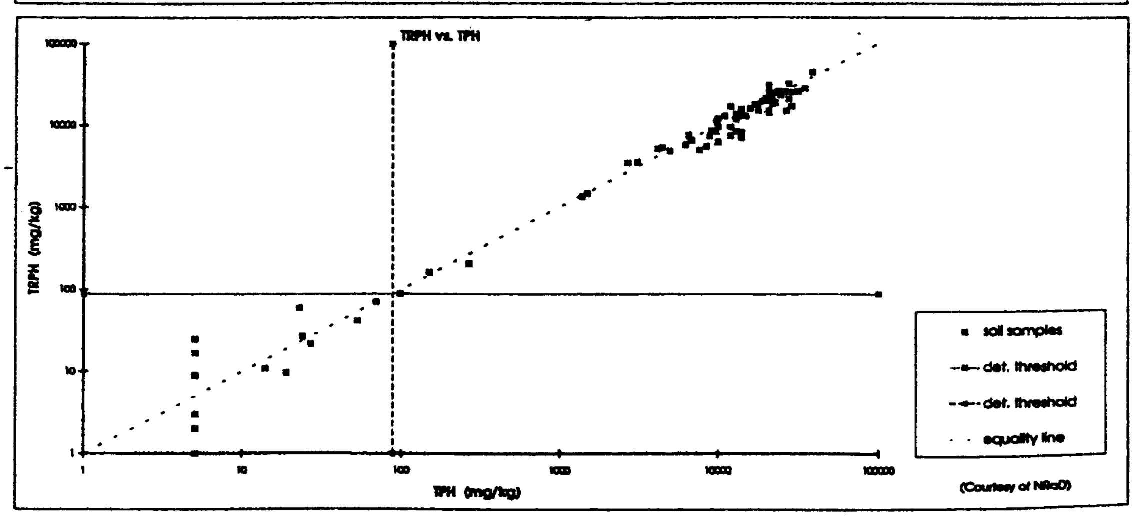
APPENDIX D

Albuquerque Demonstration

ATI Laboratory and In-Situ Fluorescence Results







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STATE OF CALIFORNIA
Department of Toxic Substances Control

CERTIFICATION No. 96-01-021

ISSUED TO: United States Department of the Navy

The Site Characterization and Analysis Penetrometer System-Laser Induced Fluorescence (SCAPS-LIF) sensor is certified as a Site Characterization Technology pursuant to California Health and Safety Code Section 25200.1.5, subject to the conditions and the limitations/disclaimer set forth in the Certification Statement as published in the California Regulatory Notice Register on July 5, 1996, Register 96, Volume No. 27-Z, pages 1282-1291. The SCAPS-LIF technology is a real-time, in situ, subsurface field screening method for petroleum, oil and lubricants (POLs) that contain Polynuclear Aromatic Compounds (PNAs). This certification is specfic to the use of the SCAPS-LIF technology as a qualitative to semi-quantitative field screening method for hydrocarbon-contaminated sites where sufficient levels of PNA fluorophores are present in the hydrocarbon matrix to exhibit significant fluorescent responses above and distinguishable from background fluorescence levels. Site-specific calibrations are required to determine the technology's applicability and detection threshold for each site. Site-specific detection thresholds typically vary from levels of approximately 100 mg/kg to over 1000mg/kg as Total Petroleum Hydrocarbons (Modified EPA Method 8015) or Total Recoverable Petroleum Hydrocarbons (EPA Method 418.1). The technology is applicable to a variety of sites contaminated by POLs, including diesel fuel marine, diesel no. 2, and JP-5.

The term of the Certification shall be for a period of three (3) years from the effective date unless otherwise specified in Title 22, California Code of Regulations or revoked prior to that date for cause.

Effective Date: August 5, 1996

James M. Strock
Secretary for Environmental Protection

Jesse R. Huff
Director, Department of Toxic Substances Control

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